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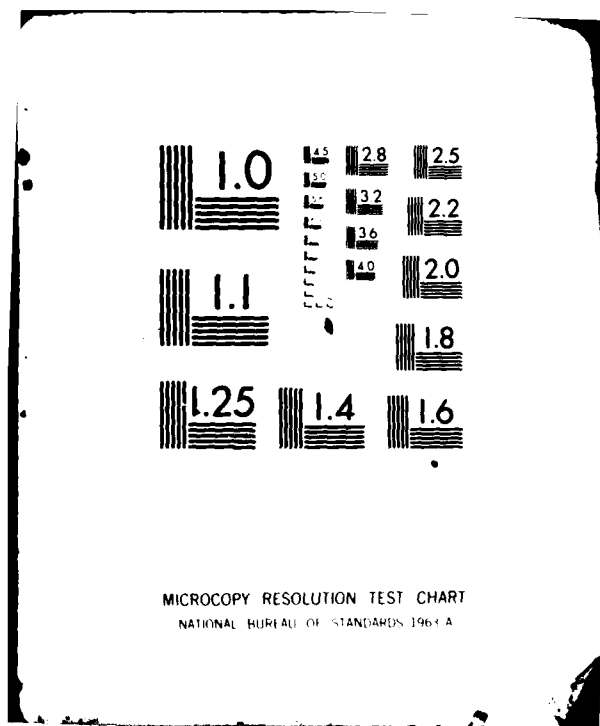
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KINETICS OF OXIDATION REACTIONS INVOLVING

B AND Al CHALCONIDES

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Work on various problems in solid and air-breathing rocket development, e.g., submicron particulate formation, requires the input of kinetic data over wide temperature ranges on the oxidation reactions of refractory free radical species. Various approaches for producing these species and investigating their kinetics, using laser-induced fluorescence and high-temperature fast-flow reactors, are discussed. To demonstrate the feasibility of a new discharge-flow reactor method for producing such radicals for kinetic studies, the kinetics of $BO + O_2 \rightarrow BO_2 + O$ was investigated. A rate coefficient of 4×10^{-12} cm^3 $molecule^{-1}$ at 295 K

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I. INTRODUCTION - SCIENTIFIC OBJECTIVES

The need for a reliable kinetic data base on reactions of refractory metal atoms, metal oxide radicals and metal halide radicals* for various aspects of solid and air breathing rocket development has frequently been expressed, e.g. Ref. 1. To provide such data for metal atoms, one of us (AF) previously developed the HTFFR (High-Temperature Fast-Flow Reactor) technique,[2-4] which is uniquely useful for measuring rate coefficients and their temperature dependence within the temperature range of approximately 300 - 1900 K. Some data on a metal oxide radical, AlO, were also obtained through the convenient expedient of observing the two-step oxidation of Al atoms with the same oxidiser. However, the need for more systematic means of studying reactions of metal radicals in HTFFRs was obvious[4]. The visit, during the grant year, of AF to the laboratory of the other of us (MAAC), with its state-of-the-art equipment for laser-induced fluorescence (LIF) detection of free radicals, presented a natural opportunity for such more systematic exploration. LIF currently represents the most sensitive technique for monitoring of such radicals. Consequently, the objectives for this program were to make a kinetic study of a reaction of a refractory oxide radical ($BO + O_2 \rightarrow BO_2 + O$)

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*The word "metal" is used here in its propulsion technology sense, thus specifically including B, which is not a metallic element in the usual physico-chemical sense.

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and to explore means for future kinetic studies of refractory radical species of significance to Air Force development programs.

II. BIBLIOGRAPHY OF PUBLICATIONS

The present one year effort has resulted in the following publication (Appendix A of this report):

I. P. Llewellyn, A. Fontijn and M. A. A. Clyne, "Kinetics of the Reaction $BO + O_2 \rightarrow BO_2 + O$", Chemical Physics Letters, in press.

"The reaction of $BCl_3 + N + O$ was used to produce $BO\ X^2\Sigma^+$ radicals for study in a fast-flow reactor. Laser-induced fluorescence was used to follow the $BO\ X^2\Sigma^+$ radicals. The feasibility of kinetic studies on these radicals was demonstrated through a kinetic study of the $BO + O_2$ reaction, giving a rate coefficient k_1 equal to $((4.4^{+4.7}_{-3.2}) \times 10^{-12}\ cm^3$ molecule^{-1} s^{-1} at 295 K."

Additionally considerable progress was made in the preparation of a book chapter which discusses the status of theory, experiments and predictive ability on the influence of temperature on rate coefficients of bimolecular reactions. The type of metal and metal radical reactions of interest to the Air Force form an important subset of the reactions discussed. This chapter and book are scheduled for publication in late 1982. The reference will be:

A. Fontijn and R. Zellner, "Influence of Temperature on Rate Coefficients of Bimolecular Reactions" in Reactions of Small Transient Species (M. A. A. Clyne and A. Fontijn, Eds.), Academic Press, London, Chap.2.

"Kinetic studies in recent years covering wide
temperature ranges, have shown that the traditional expec-
tations of near-Arrhenius behaviour, $k = A\,T\,\exp(-E_a/RT)$,
are often unwarranted. Available data are reviewed in the
light of current theoretical and semi-empirical understanding."

III. DISCUSSION

The major complete results of the present work are
given in a publication (Appendix A). In addition to
providing an important rate coefficient, this work has
demonstrated the practicality of a chemical production
method for a highly refractory oxide species (BO),
compatible with its subsequent kinetic studies in a
fast-flow reactor. This demonstration was made for one
species using a room temperature reactor. The two obvious
questions raised for future work thus are:

(i)   what is the temperature range for which this type
      of approach can be used, and

(ii) how can other radicals similarly be studied?

A.   Temperature range

Figure 1 shows a simple means for extending the
temperature range of the studies. Compared to the work of
Appendix A, the Pyrex reactor has been replaced by a ceramic
reactor, surrounded by a high temperature furnace. At the
upstream end the free radical species (MeX) flows in from a
preparation line, which for BO would be identical to that of
the present work. Any desired oxidant O_2, CO_2, NO_2, HCl,
etc. can be introduced, generally independent of the MeX
production method. An HTFFR based on this model was

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designed, constructed and tested during the course of the
grant, but insufficient time was available to study the
BO/O_2 reaction in this apparatus. The reaction tube and BO
inlet were made from impervious mullite (Morgan Refractories
Ltd.) and the three-zone furnace was made of Kanthal-A
elements (Bulten-Kanthal AB) surrounded by Triton blanket
and board insulating material (Morgan Refractories Ltd.).
This combination of materials allows work up to about 1500
K. The observation fluorescence cell was replaced outside
the heated zone. This was done to facilitate joining of the
reactor to existing laser-induced fluorescence apparatus at
Queen Mary College, not because of a principal advantage. A
previously used[3,4] modular HTFFR is shown in Figure 2. It
is obvious that the "source section" of that reactor can be
removed and the reactor section joined to a preparation line
as in Figure 1, resulting in a constant high temperature
zone including the observation region.

Thus there appears to be no reason in principle why the
metal radical work could not be extended over the full
temperature range of some previous HTFFR work (300 - 1900 K)[3,4].
The choice of apparatus design will depend on the radical of
interest, as will be discussed now.

B. Production and monitoring of further radical species

The traditional way of producing metal oxide and halide
radical species is by evaporation of inorganic compounds[5].
This approach could be practised with an original[3,4] modular
HTFFR, Figure 2, in which the vaporizer contains the

inorganic parent compound. Thus, SnO can be produced by dissociative evaporation of SnO_2, or else from Sn/SnO_2 mixtures where the Sn acts as a reducing agent; these methods can be used at about 1400 K[6]. Such vaporization methods are in principle similar to those used in metal atom HTFFR work[3,4].

A number of methods for refractory radical production have been developed in recent years in the area of preparative metal-organic chemistry. These can best be utilized with a preparation line approach, Figure 1. They can be divided into two groups: gas-solid reactions and pyrolysis[5,7]. An example of the former is the production of BF by passage of BF_3 through solid B granules at ~ 2000 K, and one of the latter is the production of BCl by passing B_2Cl_4 through a quartz tube at ~ 1300 K (also yielding BCl_3). In HTFFR studies it is of course necessary to ascertain that the other species present, BF_3 and BCl_3 in these examples, do not interfere with the reactions studied, which is in general not likely for such thermally rather stable compounds. These groups of methods can be expanded by the use of laser photolysis, a method apparently not yet used in studies of reactions of inorganic free radicals, but one for which the basic technology has reached a high degree of development in recent years[8,9].

It is important to note that neither the literature on evaporative, nor on the preparative, methods appears to

contain any information on the production of BO, the species investigated experimentally in the current study (Appendix A). Only B_2O_2 could be produced in metal-organic synthesis work[7]. The discharge-flow reaction method developed here for BO, i.e. reacting BCl_3 with a flow of $N/O/N_2$, was attempted on the basis of observations that BO emission spectra can be produced in the reaction of BCl_3 with active nitrogen containing traces of oxygen[10], while the reaction of BCl_3 with O/O_2 mixtures only appears to produce BO_2.[11] For many radicals such emission spectroscopic observations[10] could be adapted to discharge-flow methods for production of their respective ground states. Often the yields will be very low, as was found to be the case for BO. However, coupled with the extremely sensitive monitoring method, which is LIF, low radical concentrations need not be a drawback.

In the above we have emphasised the preparation and monitoring of diatomic radicals. However, triatomic radicals can be produced by similar methods and again LIF offers currently the most sensitive detection technique. For these larger species there is currently less information available from earlier work. That this situation is changing may be illustrated from the above mentioned BO_2 studies[11] and the recent work by Hirota[12] on BOCl.

IV. CONCLUSIONS

In this work the practicality of producing a highly refractory free radical species, BO, by a preparation line

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method has been demonstrated and k..netic data on its reaction with O_2 have been obtained. The technical possibilities for more extensive studies of rate coefficients, and their temperature dependence, for refractory radical species of Air Force interest are highly promising. A large variety of radical production methods can be combined with HTFFR methodology and laser-induced fluorescence monitoring to achieve this goal.

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OXIDANT

MeX + BATH GAS

BATH GAS

FURNACE

FLUORESCENCE CELL

BAFFLE ARM

WINDOW

PUMP
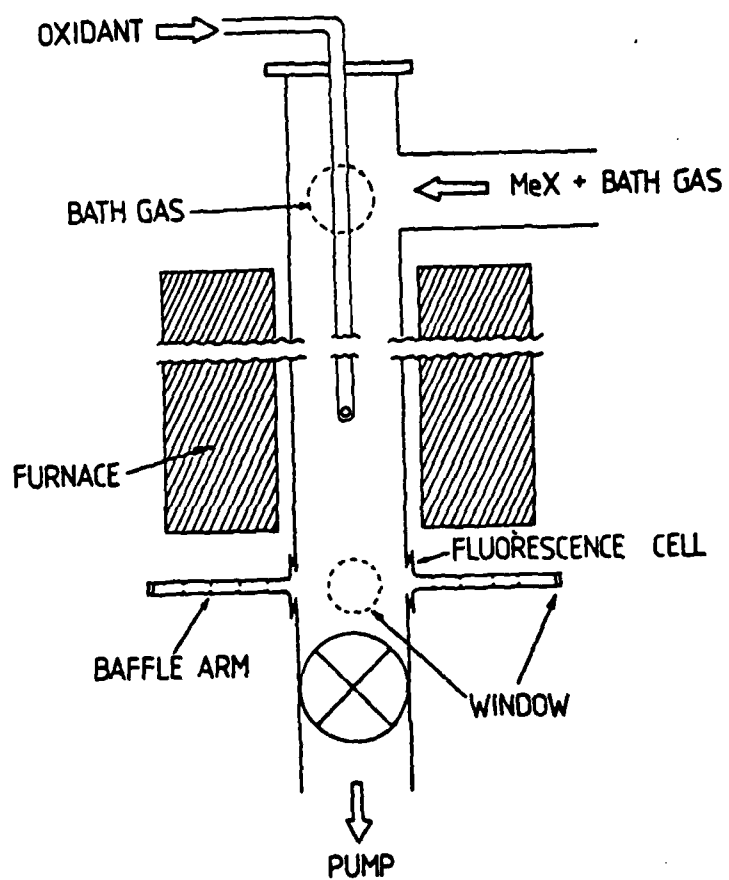
<u>Figure 1</u>   Schematic of a modular HTFFR with preparation line metal radical
source.

OXIDANT

PUMP

WINDOW

REACTOR
SECTION

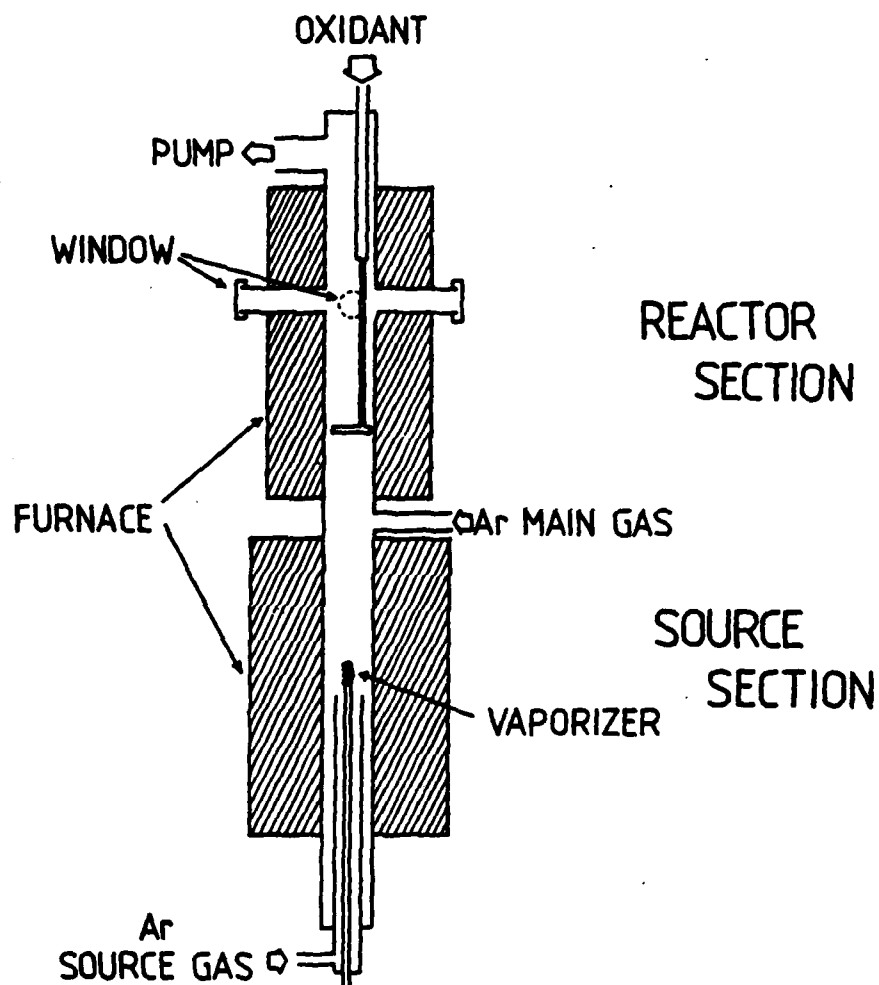FURNACE

Ar MAIN GAS

SOURCE
SECTION

VAPORIZER

Ar
SOURCE GAS

Figure 2   Schematic of a modular HTFFR with a high temperature source section

for evaporative introduction of metal radicals or atoms.

KINETICS OF THE REACTION BO + O_2 → BO_2 + O

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No. of tables: 1

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ABSTRACT

The reaction of BCl_3 + N + O was used to produce BO $X^2\Sigma^+$ radicals for study in a fast-flow reactor. Laser-induced fluorescence was used to follow the BO $X^2\Sigma^+$ radicals. The feasibility of kinetic studies on these radicals was demonstrated through a kinetic study of the BO + O_2 reaction, giving a rate coefficient k_1 equal to $(4.4^{+4.7}_{-3.2}) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 295 K.

1. Introduction

The development of the HTFFR (high-temperature fast-flow reactor) technique [1] has led to a number of measurements of rate coefficients k(T) for reactions of refractory metal atoms over wide temperature ranges*. In that work metal atoms were produced by evaporation, and their oxidation reactions studied in a contiguous section of the flow tube. Little systematic work has been done to obtain similar k(T) data for reactions of free radicals of refractory species, though the study of the Al + O2 reaction has allowed rate coefficient measurements of the subsequent reaction of AlO + O2 in the same flow tube [3]. An observation of the similar sequence Al + SO2, AlO + SO2 also has been reported [4]. Some metal oxide and halide radicals probably could be produced directly in an HTFFR by evaporative methods [5], to allow study of their reactions with various oxidisers, as in the metal atom work. An alternative approach is to produce such radicals upstream from the flow tube in a side arm by one of a number of methods (e.g. gas phase reactions, multiphase reactions, pyrolysis, photolysis). Such techniques have to be capable of producing a continuous, controllable flux of the refractory radicals over a period of several hours, to be practical for flow tube measurements. Light et al [6] have recently demonstrated the feasibility of such an approach for BF, produced by the reaction of a BF3/Ar flow with boron granules at T > 1800 K [6].

The radical BO is a notoriously difficult species to produce with any appreciable flux; the dimer B2O2 is more readily obtained [5,7]. However, we now report the successful generation and detection of BO in a flow reactor, and in order to establish the feasibility of kinetic measurements

*For a review and data summary see Ref. [2], in which other observations on metal atom kinetics are also discussed.

on this radical, we present kinetic data for the reaction,

$$BO + O_2 \rightarrow BO_2 + O \qquad \ldots(1)$$

studied by laser-induced fluorescence (LIF).

The approach followed was to produce BO in a side arm of the flow tube reactor by the gas phase reaction of N-atom/O-atom mixture with BCl3 at room temperature. This reaction system has previously been used successfully in this laboratory for LIF observations on the spectroscopy and radiative lifetimes of the BO radical in the excited $A^2\Pi$ state [8]. The high fluorescence yield and relatively short radiative lifetime ($\tau_{rad} \approx 1$ to 2 μs) of BO $A^2\Pi$ combine to make LIF a sensitive probe of the relative concentrations of ground-state $X^2\Sigma^+$ BO. In addition, by accurate tuning of the laser frequency, LIF can be made completely selective for BO and completely insensitive to contaminants (e.g. BO2). However the BO radical concentrations obtained here were low; hence, signal-to-noise ratios for the detection of BO were limited, and the resulting rate coefficient was not as accurate as would have been desired, but still adequate to allow comparison with the corresponding AlO reaction.

2. Apparatus and procedure

A schematic of the apparatus is shown in figure 1. A $N + O \rightarrow N_2$ mixture, produced in the usual way from a microwave discharge in N2 with partial NO titration, reacted in the side arm with BCl3 to produce BO. The BCl3 was introduced through a downstream nozzle near the junction with the reaction tube. This NO terminated the BO production by complete titration of the N atoms, as indicated by the disappearance of the intense blue BO chemiluminescence beyond this point. Additional bath gas, Ar, was introduced to the reaction tube to obtain the fast average flow velocities necessary for adequate transport of BO. O2 was introduced through a variable position

nozzle.

The reaction tube was of 19 mm bore and was 370 mm in length from the side arm to the fluorescence cell. A single stage 240 m³ h⁻¹ vacuum pump (Edwards Model 240/30) was used. All permanent gases were standard grade. NO was purified by passage through activated alumina and KOH. BCl_3 was obtained as gas from a storage reservoir into which it was distilled from the liquid (BDH, purity > 98%) and diluted with Ar. The volume flow rates of N_2, Ar and O_2 were measured by the inverted burette method; those of BCl_3 and NO were not measured accurately. Pressure was measured after each experiment with a transducer (MKS Baratron 221) connected to a movable pressure probe [2]. During the experiment the transducer was connected to the fluorescence cell.

All kinetic measurements were made under pseudo first-order conditions, i.e., with $[O_2] \gg [BO]$, using the O_2 inlet at a number of fixed positions (times) and at which $[O_2]$ was varied. Appreciable BO destruction on the O_2 inlet tube and reactor walls prevented the making of measurements at fixed $[O_2]$ values with varying time (nozzle position). This BO destruction rate decreased somewhat as a thin white film of reaction products deposited on the walls in the course of the work. The relative BO concentration was monitored by pumping the (0,0) Q1 head of the $A^2\Pi - X^2\Sigma^+$ transition at 425 nm. The resulting fluorescence was focussed onto a slit, and detected with a photomultiplier (S20 cathode, EMI 9816B, 2 ns rise time) through a filter transmitting at $\lambda > 500$ nm. The laser apparatus used has been described previously [8]. Tripled Nd-YAG output was used to produce radiation near 425 nm from an oscillator-amplifier design of dye laser, using Stilbene 420 dye. A 0.01 nm band-width and a repetition rate of 20 Hz were used, giving an average pulse energy of 300 µJ with pulse-to-pulse jitter < 5%.

Only low fluorescence intensities were obtained (indicating very low [BO]), requiring the careful minimization of cw light originating from the BO production reactions in the side arm of the flow tube. The most primitive method for measuring pulsed LIF intensities, namely, with a boxcar integrator, failed to give a reliable measurement of relative BO concentration. Instead, the pulsed fluorescence signals were digitized in real time using a fast transient recorder (Biomation 6500, 6 bit, > 2 ns channel, 1024 channels) coupled to a minicomputer (Nicolet LAB-80). This allowed data collection over many shots (typically > 1000) and reduced the laser shot-to-shot noise to a negligible level. Care was taken to use a sufficiently high PMT voltage (1900 V) to ensure proper digitisation of the signal. This was verified by subtracting the background from the decays and ascertaining that the logarithms of the resulting intensities yielded straight lines, when plotted with time.

The data were analysed using the minicomputer. The area under each decay curve was computed by averaging a set number of time channels following the laser pulse. The average cw background was determined from a number of channels recorded before initiation of the laser pulse, and was subtracted from the integrated signal. As a check on this procedure, BO was removed by using an excess of O_2, under which conditions negligible integrated signals indeed were obtained. In addition the number of channels used in the integration was varied and were found to have negligible effect (< 10% change) on the final value of the rate coefficient. Negligible shortening of the lifetime (due to quenching) was observed upon addition of O_2 in the concentration range used. The slopes of $\ln(F^0_{RO}/F_{BO})$ vs $[O_2]$ plots yielded the product kt [2]:= $\ln(F^0_{RO}/F_{RO}) = -kt$, noting that F_{RO} is the fluorescence intensity at a given $[O_2] > 0$, and F^0_{RO} is the intensity

In the absence of O_2. Under the conditions used (see Table I), the flow profile was intermediate between plug and parabolic flow. Exact treatment of this intermediate case was complicated by the need to have good measurements of the rate of removal of the BO on the walls of the flow tube [9]. This rate was found to be very fast, but could not be obtained accurately. Therefore a simplified method was employed by which the measured rate coefficient is multiplied by a factor equal to 1.6 x 1/1p, where 1p is the distance required for full parabolic flow to develop and 1 the distance of the O_2 inlet to the centre of the fluorescence cell. Within experimental error, this was found to be equivalent in most cases to multiplying the experimental rate coefficient values by 1.3 [2,3], or by applying the method due to Iannuzzi and Kaufman [10].

3. Results

The rate coefficient measurements are summarised in Table I. The results may be seen to be independent of the experimental parameters. The plots of $\ln(F^o_{BO}/F_{BO})$ against $[O_2]$ plots mostly approximated to straight lines well (correlation coefficient R in the range -0.90 to -0.99). A few experiments had R < 0.8 and were rejected. The mean value, and the standard deviation of the measurements is $(4.4 \pm 3.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Estimating systematic uncertainties to be 20%, including 10% for uncertainty in the flow profile factor, the recommended k_1 is $(4.4^{+4.7}_{-3.4}) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.

The reaction product BO_2 of the $BO + O_2$ reaction, was identified using a cw laser (Coherent 599-21) and photon counting equipment. The fluorescence of the BO_2 was monitored at $\lambda > 560$ nm, whilst exciting the

$A^2\Pi - X^2\Pi$ (00°0 - 00°0) band at 547 nm. As O_2 was added, the BO_2 signal increased at a rate compatible only with the above magnitude of k_1. However, no attempt was made to measure the value of k_1 of the $BO + O_2$ reaction in this way, since it was evident that the BO_2 so formed itself was rapidly removed.

4. Discussion and Conclusions

A rate coefficient $k_1 = (4.4^{+4.7}_{-3.4}) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ thus has been obtained at room temperature for the slightly exothermic (~ 40 kJ mol⁻¹) [11] reaction (1). This value for the $BO + O_2$ reaction may be compared to the corresponding reaction (2) of the next heavier Group IIIA element,

$$AlO + O_2 \rightarrow AlO_2 + O \qquad \qquad ...(2)$$

for which HTFFR experiments yielded $k(T) = (2.3 \pm 0.6) \times 10^{-13} \exp[(333 \pm 170)/T]$ from 300 to 1400 K [3], or $(7.2 \pm 3.6) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 300 K. Both the dioxides BO_2 and AlO_2 have in their stable ground-state form a symmetrical linear structure [11]. Reaction (1) thus appears to be considerably faster than reaction (2), notwithstanding the much higher ionization potential of the central atom (8.30 eV for B, as against 5.92 eV for Al) [12], and the expected shorter available interaction distance. The low Arrhenius A factor and small negative temperature-dependence of reaction (2) may be attributed [3,13] to formation of a bound intermediate complex which can with high probability redissociate to the reactants. The larger value of k_1 may thus indicate a direct reaction path (or at least a smaller probability for redissociation of a hypothetical complex), possibly related to the more covalent character of the new bond. This would suggest a more positive temperature dependence

for reaction (1) than for reaction (2).

To determine any such temperature dependence, the side-arm preparation method used here could readily be combined with an HTFFR apparatus. In general, this type of technique for production of radicals of refractory species allows for determinations of absolute rate coefficient values of reactions of the radicals with a variety of second reactants, independently of the initial radical production method; the need for such development has been discussed [2]. For several refractory radical species, methods for production, at much higher fluxes than could be achieved here for BO, are known [5,14].

Acknowledgement

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Summary of BO + O_2 → BO_2 + O Rate Coefficient Measurements

P (Torr)[a]	N_2 flow (cm^3(STP)s^{-1})	Ar flow (cm^3(STP)s^{-1})	$\bar{v}$[b] (m s^{-1})	t (ms)	$[O_2]$ (10^{12} cm^{-3})	F^0_{BO} [c] (arbitrary units)	k (10^{-12} cm^3 molecule^{-1} s^{-1})	R
2.8	16	67	89	2.2	0.6 – 20	0.18	3.9	-0.96
2.7	16	67	90	3.1	3 – 34	0.20	9.6	-0.99
2.3	16	33	50	5.5	1 – 14	0.23	1.1	-0.99
2.9	16	67	87	2.9	8 – 21	0.23	3.7	-0.90
2.8	16	33	53	5.5	7 – 13	0.40	0.7	-0.97
2.8	16	33	53	5.9	5 – 22	0.43	4.3	-0.98
2.8	16	33	53	6.1	3 – 40	0.54	1.8	-0.94
2.8	16	33	53	4.8	2 – 40	0.62	1.5	-0.98
2.7	15	18	37	7.0	3 – 40	0.46	0.7	-0.86
2.8	15	18	35	9.1	2 – 50	1.0	1.5	-0.98
2.6	27	18	51	6.0	4 – 50	1.0	7.4	-0.81
2.6	27	18	52	5.2	4 – 25	0.30	7.5	-0.98
2.6	27	18	52	4.8	2 – 23	0.41	3.7	-0.99
2.5	27	18	53	4.3	2 – 30	0.39	10.6	-0.96
2.7	28	35	69	3.5	0.7 – 4	0.12	9.3	-0.95
1.9	22	18	65	3.7	2 – 20	0.20	7.7	-0.99
2.0	22	18	60	5.3	0.7 – 4	0.14	8.6	-0.93
4.1	22	18	30	9.3	2 – 12	0.23	1.9	-0.91
4.0	22	18	30	7.9	2 – 20	0.12	5.0	-0.94
4.1	22	18	30	6.7	4 – 40	0.13	5.6	-0.90
5.5	22	96	64	1.2	1 – 20	0.29	2.2	-0.96
5.5	22	96	64	3.6	2 – 13	0.64	2.0	-0.99
5.5	22	96	65	2.9	1 – 17	0.89	1.0	-0.89

[a] 1 Torr = 133.3 Pa   [b] mean plug flow velocity   [c] initial BO fluorescence intensity

GXUAAJ
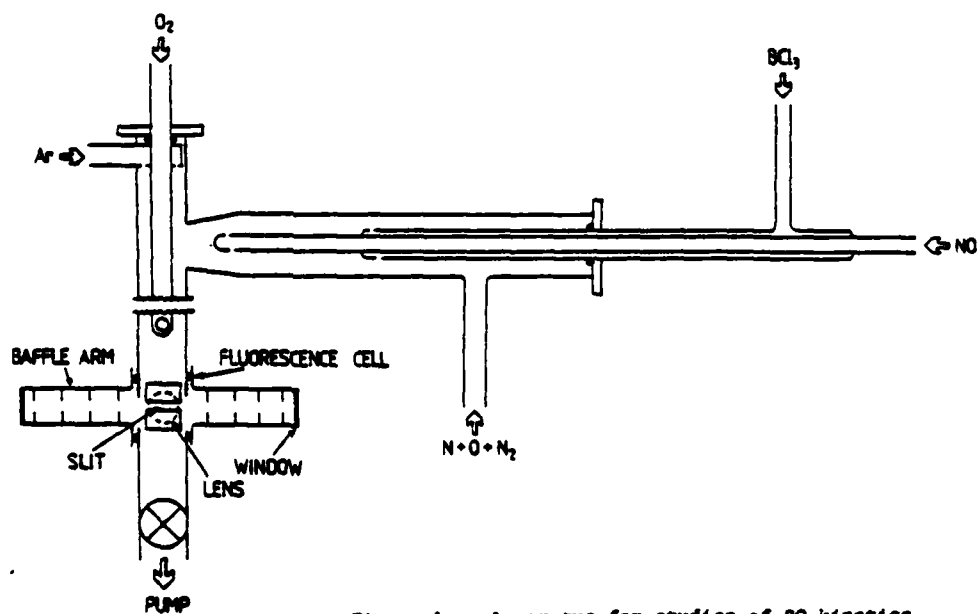
Figure 1   Apparatus for studies of BO kinetics.

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